

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
15 February 2001 (15.02.2001)

PCT

(10) International Publication Number
WO 01/10643 A1

(51) International Patent Classification⁷: **B32B 27/32**

29640 (US). CHILDRESS, Blaine, C. [US/US]; 300 Mountain View Lane, Inman, SC 29349 (US). BUC-CULO, Adam, D. [US/US]; 222 Libby Lane, Mauldin, SC 29332 (US).

(21) International Application Number: **PCT/US00/21483**

(74) Agents: QUATT, Mark, B. et al.; Cryovac, Inc., 100 Rogers Bridge Road, P.O. Box 464, Duncan, SC 29334 (US).

(22) International Filing Date: 7 August 2000 (07.08.2000)

(25) Filing Language: English

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:

60/148,445 11 August 1999 (11.08.1999) US
09/564,177 3 May 2000 (03.05.2000) US

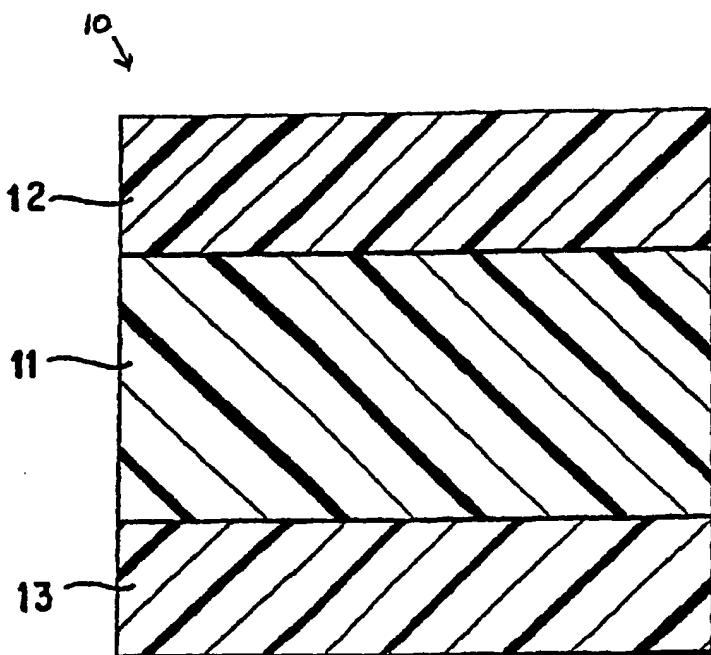
(71) Applicant (*for all designated States except US*): SEALED AIR CORPORATION (US) [US/US]; Park 80, East, Saddle Brook, NJ 07663 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): BANASZAK, Cheryl, M. [US/US]; 108 Glendale Lane, Easley, SC

[Continued on next page]

(54) Title: HEAT SHRINKABLE FILM WITH MULTICOMPONENT INTERPENETRATING NETWORK RESIN



(57) Abstract: An oriented heat shrinkable film includes a layer including a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin including a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component with a melt index of between 1.5 and 20; the film having a haze value (ASTM D 1003-95) less than or equal to 5, a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM D 2732-83) at a temperature of 200 °F of at least 8 % in either or both of the longitudinal and transverse directions. Films with substantially balanced free shrink are preferred, in particular those with a free shrink balance of less than or equal to 30 %. Advantages in downgauging and/or mechanical properties are provided without substantially adversely affecting properties such as free shrink and optics.

WO 01/10643 A1



Published:

— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

HEAT SHRINKABLE FILM WITH MULTICOMPONENT INTERPENETRATING
NETWORK RESIN

Field Of The Invention

5 The present invention relates to oriented, heat shrinkable thermoplastic film.

Background Of The Invention

For many years, the heat shrinkable films industry has endeavored to reduce film gauge while maintaining performance in response to initiatives associated with 10 source reduction. Lower gauges also allow for increased footage on rolls, which benefits the customer by reducing downtime (changeover time).

However, prior strategies involving films having single resin layers or conventional melt blends of resins, especially linear low density polyethylene (LLDPE), typically resulted in performance concessions. For instance, some improvement in optical 15 quality and percent free shrink may have been seen, but with an undesirable degradation in impact strength. In the case of other blend compositions, good impact resistance and abrasion resistance could be obtained, but with an accompanying degradation in free shrink and clarity.

Thus, the technical challenge remained to design display films with higher impact resistance than LLDPE, but with optical and shrink properties comparable to 20 LLDPE. The inventors have found that the use of a multicomponent ethylene/alpha-olefin interpenetrating network resin (herein "IPN resin") permits property tailoring without compromising clarity, impact resistance, free shrink, or resistance to tear propagation. The result is a stronger, more abuse resistant film having the shrink and 25 optical properties presently provided by LLDPE. These inventive films result in lower failures at a processor's packaging machine, or during distribution of contents. The tensile strength of this film is superior to many conventional films, thereby permitting downgauging. A downgauged film with performance properties comparable to prior LLDPE formulations at their previous gauge can account for less downtime and 30 changeovers at the customer's plant owing to the above mentioned greater roll footage. The ability to deliver higher value heat shrinkable film without a significant cost premium is a distinct advantage of the films of this invention. Other resins recognized for providing certain performance features (i.e. clarity, seal initiation temperature, low temperature shrink) such as metallocene resins, or blends, cannot provide abrasion 35 resistance, nor deliver low temperature and low haze performance without a substantial cost penalty. The inventors have found that the use of an IPN resin in the skin

layer or layers of a multilayer film can result in reduced levels of required antiblocking agent via removal of, or reduction in, the need for ethylene/vinyl acetate copolymer (EVA) in the skin layers. Additive reduction is advantageous because of reduced abrasive damage from inorganic particles, reduced accumulation of wax onto machine 5 and package contents due to transfer from film to contact surfaces, together with better gloss and clarity.

The use of IPN resins thus provides superior mechanical strength properties while preserving excellent optical and shrink values comparable to e.g. D955™ film. These performance attributes can lead to higher performance films at comparable 10 thickness relative to current LLDPE films or to thinner films.

An improved packaging film in accordance with the present invention can thus provide adequate resistance to tear propagation; excellent free shrink; good optics, including haze, clarity, and gloss values; high impact resistance; and high tensile strength.

15

Summary Of The Invention

In a first aspect, a multilayer oriented heat shrinkable film comprises an internal layer comprising a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin comprising a homogeneous 20 component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component having a melt index of between 1.5 and 20; and outer layers comprising a polymeric resin; wherein the film has a haze value (ASTM D 1003-95) less than or equal to 5, a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM D 2732-83) at a temperature of 200°F 25 of at least 8% in either or both of the longitudinal and transverse directions.

In a second aspect, a multilayer oriented heat shrinkable film comprises an internal layer comprising polymeric resin; first and second intermediate layers, each disposed on a respective opposite side of the internal layer, comprising multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, 30 the resin comprising a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component having a melt index of between 1.5 and 20; and first and second outer layers, disposed on the first and second intermediate layers respectively, comprising a polymeric resin; wherein the film has a haze value (ASTM D 1003-95) less than or equal to 5, a peak 35 load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM

D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.

In a third aspect, a solid state oriented heat shrinkable film comprises between 50 and 100 percent, by volume of the total film, of a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin comprising

5 a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component having a melt index of between 1.5 and 20; and between 0 and 50 percent, by volume of the total film, of a polymeric resin; wherein the film has a haze value (ASTM D 1003-95) less than or equal to 5, a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.

In a fourth aspect, a multilayer oriented heat shrinkable film comprises an

10 internal layer comprising a blend of a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, and ethylene polymer or copolymer having a density of at least 0.935 grams/cubic centimeter, wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 comprises a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component with a melt index of between about 1.0 and 20; and outer layers comprising a polymeric resin; wherein the film has a haze value (ASTM D 1003-95) less than or equal to 5, a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the

15 longitudinal and transverse directions.

Definitions

"Acrylic" herein refers to acrylic or to methacrylic.

"Composite free shrink" herein refers to a value determined by summing the

30 percent free shrink in the longitudinal direction with the percentage free shrink in the transverse direction. For example, Example 1 in Table 3 displays the following values at 200°F: 17% free shrink in the longitudinal direction, and 19% free shrink in the transverse direction. The composite free shrink would then be 17% + 19%, or a value of 36%.

35 "CRYSTAF" herein refers to an analytical technique which can be used to characterize the composition of a polymer by means of a fractionation scheme based

on crystallization isolation. Samples were analyzed by Polymer Char (Valencia Parc Tecnologic, PO Box 176 E-46980, Paterna, Spain). The technique generates results equivalent to that provided from TREF. (see Monrabal (1994) J. Applied Poly. Sci. 52, 491; Soares et al., SPE Polyolefins XI p287-312).

5 "Ethylene/alpha-olefin copolymer" (EAO) herein refers to copolymers of ethylene with one or more comonomers selected from C₄ to C₁₀ alpha-olefins such as butene-1 (i.e., 1-butene), hexene-1, octene-1, etc. in which the molecules of the copolymers comprise long chains with relatively few side chain branches. This molecular structure is to be contrasted with conventional high pressure low or medium density polyethylenes
10 which are more highly branched than their respective counterparts. EAO includes such heterogeneous materials as linear medium density polyethylene (LMDPE), linear low density polyethylene (LLDPE), and very low and ultra low density polyethylene (VLDPE and ULDPE), such as DOWLEX™ or ATTANE™ resins supplied by Dow, ESCORENE™ or EXCEED™ resins supplied by Exxon; as well as homogeneous
15 ethylene/alpha olefin copolymers (HEAO) such as TAFMER™ resins supplied by Mitsui Petrochemical Corporation, EXACT™ resins supplied by Exxon, AFFINITY™ resins supplied by the Dow Chemical Company, or ENGAGE™ resins supplied by DuPont Dow Elastomers. HEAO resins also include long chain branched homogeneous ethylene/alpha-olefin copolymers.

20 "Free shrink balance" herein refers to the value, which defines the percent of difference between the free shrink of a film in the longitudinal direction and the free shrink of the same film in the transverse direction at 240°F, defined by the mathematical relationship:

$$\frac{[FS_{TD} - FS_{LD}]}{FS_{TD}}$$

25 where:
FS = free shrink
TD = transverse direction
LD = longitudinal direction

30 Films of the present invention preferably exhibit a free shrink balance of less than or equal to 30%. As an example (see Table 3) the free shrink of Example 1 in the longitudinal direction is 43% at 240°F. The free shrink of Example 1 in the transverse direction is 48% at 240°F. Inserting these values in the above relationship:

[48 - 43]

48

i.e., the absolute value of 48 minus 43 equals 5, and 5 divided by 48 equals .104, which is equivalent to 10.4%, which is less than 30%.

5 "Heat shrinkable" herein refers to a property of a material which, when heated to a temperature of 200°F, will exhibit a free shrink (ASTM D 2732-83) of at least 8% in the longitudinal direction, and/or at least 8% in the transverse direction. Heat shrinkable films of this invention are solid state oriented as contrasted to hot blown films which are melt state oriented.

10 "High density polyethylene" (HDPE) herein refers to a polyethylene having a density of between 0.94 and 0.965 grams per cubic centimeter.

"Intermediate" herein refers to a layer of a multi-layer film which is between an outer layer and an internal layer of the film.

15 "Internal layer" herein refers to a layer which is not an outer or surface layer, and is typically a central or core layer of a film.

"LD" herein refers to the longitudinal direction, i.e. the direction of the film parallel to the path of extrusion. "TD" herein refers to the transverse direction, i.e. the direction of the film transverse to the path of extrusion.

20 "Linear low density polyethylene" (LLDPE) herein refers to polyethylene having a density between 0.916 and 0.925 grams per cubic centimeter.

"Linear medium density polyethylene" (LMDPE) herein refers to polyethylene having a density between 0.926 grams per cubic centimeter and 0.939 grams per cubic centimeter.

25 "Multicomponent ethylene/alpha-olefin interpenetrating network resin" or "IPN resin" herein refers to multicomponent molecular mixtures of polymer chains. Because of molecular mixing, IPN resins cannot be separated without breaking chemical bonds. Polymer chains combined as IPN resins are interlaced at a molecular level and are thus considered true solid state solutions. Interpenetrating networks, unlike blends, become new compositions exhibiting properties distinct from parent constituents. Interpenetrating networks provide phase co-continuity leading to surprising enhancement of physical properties. Due to the mixture of at least two molecular types, these compositions may exhibit bimodal or multimodal curves when analyzed using TREF or CRYSTAF. Interpenetrating networks as herein used includes semi-interpenetrating networks and therefore describes crosslinked and uncrosslinked mul-

ticomponent molecular mixtures having a low density fraction and a high density fraction. Specific production methods for preparing IPN resins useful for carrying out the present invention, are disclosed in US Patent No. 5,747,594 (deGroot et al.), US Patent No. 5,370,940 (Hazlitt et al.), and WO 94/17112 (Kolthammer), all herein incorporated by reference in their entirety. Preferred IPN resins are produced from a solution polymerization scheme. Especially preferred IPN resins are prepared using a parallel or sequential multiple reactor scheme. Alternatively, IPNs useful for the inventive films may be prepared within a single reactor by completing polymerization of the heterogeneous component prior to initiating the polymerization of the homogeneous component. Examples of catalysts suitable for preparing the heterogeneous component are described in US Patent Nos. 4,314,912 (Lowery et al.), US 4,547,475 (Glass et al.), and US 4,612,300 (Coleman, III); examples of catalysts suitable for producing the homogeneous component are described in US Patent Nos. 5,026,798 and 5,055,438(Canich); 3,645,992(Elston); 5,017,714 (Welborn); and 4,076,698 (Anderson); all herein incorporated by reference in their entirety.

"Outer layer" herein refers to what is typically an outermost, usually surface layer or skin layer of a multi-layer film, although additional layers, coatings, and/or films can be adhered to it.

"Polymer" herein refers to homopolymer, copolymer, terpolymer, etc. "Copolymer" herein includes copolymer, terpolymer, etc.

"Solid-state orientation" herein refers to the orientation process carried out at a temperature higher than the highest T_g (glass transition temperature) of resins making up the majority of the structure and lower than the highest melting point, of at least some of the film resins, i.e. at a temperature at which at least some of the resins making up the structure are not in the molten state. Solid state orientation may be contrasted to "melt state orientation" i.e. including hot blown films, in which stretching takes place immediately upon emergence of the molten polymer film from the extrusion die.

"Solid state oriented" herein refers to films obtained by either coextrusion or extrusion coating of the resins of the different layers to obtain a primary thick sheet or tube (primary tape) that is quickly cooled to a solid state to stop or slow crystallization of the polymers, thereby providing a solid primary film sheet, and then reheating the solid primary film sheet to the so-called orientation temperature, and thereafter biaxially stretching the reheated film sheet at the orientation temperature using either a tubular solid-state orientation process (for example a trapped bubble method) or using a simultaneous or sequential tenter frame process, and finally rapidly cooling the

stretched film to provide a heat shrinkable film. In the trapped bubble solid state orientation process the primary tape is stretched in the transverse direction (TD) by inflation with air pressure to produce a bubble, as well as in the longitudinal direction (LD) by the differential speed between the two sets of nip rolls that contain the bubble. In 5 the tenter frame process the sheet or primary tape is stretched in the transverse direction by guiding the heat softened sheet through a diverging geometry frame while simultaneously or sequentially accelerating the sheet forward to stretch it in the longitudinal direction.

"Substantially balanced free shrink" herein refers to film of the invention characterized by a free shrink balance less than or equal to 30%. As an example, Example 1 was calculated above as having a free shrink balance of 10.4% at 240°F. Since this value is less than or equal to 30%, Example 1 has a substantially balanced free shrink at 240°F.

All compositional percentages used herein are presented on a "by weight" basis, unless designated otherwise.

Brief Description Of The Drawings

A detailed description of preferred embodiments of the invention follows, with reference to the attached drawings, wherein:

20 FIG. 1 is a cross-sectional view of a three layer film;
FIG. 2 is a cross-sectional view of a five layer film;
FIG. 3 is a CRYSTAF curve of an IPN resin suitable for use in the films of this invention;
FIG. 4 is a CRYSTAF curve of a LLDPE resin representing a prior art film resin;
25 FIG. 5 is a CRYSTAF curve of a metallocene catalyzed resin; and
FIG. 6 is a CRYSTAF curve of a high density polyethylene resin.

Detailed Description Of The Invention

Referring to FIG.1, a film 10 comprises an internal layer 11, a first outer layer 30 12, and a second outer layer 13. Outer layers 12 and 13 are preferably surface or skin layers.

Internal layer 11 comprises an IPN resin having a melt index less than 1.4. Internal layer 11 comprises at least 35%, preferably at least 50%, and more preferably 35 at least 55% by volume of the film structure. Internal layer 11 comprises between 35 35 and 98%, preferably between 60 and 98%, and more preferably between 65 and 98%

by volume of the film structure, more preferably between 70 and 98% by volume of the film structure.

Preferably, the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 is derived from a solution mixture of homogeneous ethylene/ alpha-olefin and heterogeneous ethylene/ alpha-olefin, or is produced from a solution polymerization of homogeneous ethylene/ alpha-olefin and solvent combined with a solution polymerized heterogeneous ethylene/ alpha-olefin.

5 The homogeneous ethylene/alpha-olefin component is preferably long chain branched.
The homogeneous ethylene/alpha-olefin component is preferably long chain branched.

10 Internal layer 11 can further comprise a polymeric resin such as ethylene/alpha olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/alkyl acrylate copolymer, ethylene/acrylic acid copolymer, ionomer, propylene polymer or copolymer, butylene polymer or copolymer, a second multicomponent ethylene/alpha-olefin interpenetrating network resin, high density polyethylene, or ethylene polymer or copolymer having a density of at least 0.935 grams/cubic centimeter.

15 First and second outer layers 12 and 13 respectively each comprise a polymeric resin, and preferably ethylene/alpha olefin copolymer; ethylene/vinyl acetate copolymer; ethylene/alkyl acrylate copolymer; ethylene/(meth)acrylic acid copolymer; ionomer; propylene polymer and copolymer; butylene polymer and copolymer; IPN resin different
20 in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer; a blend of the IPN resin of the internal layer with another polymeric resin, such as those identified herein; or a blend of any of these materials. The ethylene/alpha-olefin copolymer can have a density of between 0.86 and 0.96, preferably between 0.90 and 0.95, more preferably between 0.91 and 0.94, and most
25 preferably between 0.915 and 0.940 grams/cubic centimeter. Where the polymeric resin of the first and second outer layers 12 and 13 comprises an IPN resin, this resin is preferably different in composition from the IPN resin of the internal layer 11. The difference between the IPN resin of the internal layer and the IPN resin of the outer layers will typically be a difference in composition, but the difference can instead, or in
30 addition, be a difference in one or more physical properties, amount or type of additives, degree of crosslinking, or the like. Typically, non-compositional differences, for example in physical properties, will be a manifestation of compositional differences.

35 Outer layers 12 and 13 are preferably identical, but can differ from each other in composition, one or more physical properties, amount or type of additives, degree of crosslinking, or the like. For example, layer 12 can comprise an ethylene/vinyl acetate with 6% vinyl acetate, while layer 13 can comprise an ethylene/vinyl acetate with 9%

v vinyl acetate. As another example, layer 12 can comprise an ethylene/vinyl acetate with 6% vinyl acetate, while layer 13 can comprise an ethylene/alpha-olefin copolymer. Layers 12 and 13 can also differ in composition, the difference created by the presence or amount of a blend of two or more resins. As an example, layer 12 can comprise an
5 IPN resin like that of internal layer 11, and layer 13 can comprise a blend of the IPN resin of the internal layer with another polymeric resin such as one of those disclosed herein. Film structures in accordance with the invention can thus be depicted as A/B/A or as A/B/C, where A, B, and C each represent a distinct layer of a multilayer film. It may sometimes be desirable to include IPN resin in one or both of the outer layers to improve
10 abrasion resistance or provide some other functionality to the film.

In an alternative embodiment (see Figure 2), a film 20 comprises an internal layer 26, first outer layer 22, second outer layer 23, first intermediate layer 24, and second intermediate layer 25.

The internal layer 26, and outer layers 22 and 23, can comprise any of the
15 materials disclosed above for layers 12 and 13 of Figure 1.

Intermediate layers 24 and 25 each comprise IPN resin, and optionally an additional polymeric resin, as disclosed for internal layer 11 of Figure 1.

Thus, Figure 2 represents a five layer embodiment in which the internal layer 11 of Figure 1 is effectively "split" into two layers 24 and 25.

20 In a second alternative embodiment, a solid state oriented heat shrinkable film comprises between 50 and 100 percent, by volume of the total film, of a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin comprising a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and a heterogeneous component with
25 a melt index of between 1.5 and 20; and between 0 and 50 percent, by volume of the total film, of a polymeric resin; wherein the film has a haze value (ASTM D 1003-95) less than or equal to 5, a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions. The film is preferably a
30 multilayer film. The polymeric resin is preferably different in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4. The film preferably has a substantially balanced free shrink. Preferably, at least 50% by volume of the total film volume comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.
35 Preferably, the film comprises greater than 0%, more preferably greater than 0.1%, such as greater than 1%, greater than 5%, or greater than 10% by volume of the total film, of

the polymeric resin; and less than 100%, more preferably less than 99.9%, such as less than 99%, less than 95%, or less than 90%, by volume of the total film, of the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

5 The polymeric resin can comprise ethylene/alpha olefin copolymer, ethylene/vinyl acetate copolymer, ethylene/alkyl acrylate copolymer, ethylene/acrylic acid copolymer, ionomer, propylene polymer and copolymer, and butylene polymer and copolymer,.

Preferred films of the invention have substantially balanced free shrink.

Table 1 identifies the materials used in the examples and comparative examples. The remaining tables describe the formulations and/or properties of films made with these materials.

Table 1

<u>Material Code</u>	<u>Tradename or Designation</u>	<u>Source(s)</u>
A1	XUR-1567-54784-30	Dow
A2	EXACT™ SLX-9103	Exxon
A3	HiD 9659™	Chevron
A4	ENGAGE™ 8150	DuPont Dow Elastomers
A5	ATTANE™ 4201	Dow
A6	AFFINITY™ SL 1170	Dow
A7	ELITE™ 5200	Dow
A8	DOWLEX™ 2045.04	Dow
A9	DOWLEX™ 2037	Dow
A10	PE 1335™	Huntsman
A11	TAFMER™ A4085	Mitsui
A12	EXACT™ 4011	Exxon
A13	ESCORENE™ LD-318.92	Exxon
A14	XUR-1567-54453-104	Dow
A15	XUR-1567-54784-33	Dow
A16	ELITE™ 5100	Dow
A17	ELITE™ 5110	Dow
A18	-----	Dow

A1 is an IPN resin with a density of 0.92 grams/cc, and a melt index of 0.75.

15 A2 is a single site catalyzed ethylene/1-hexene/1-butene terpolymer with a density of 0.901 grams/cc, and a melt index of 2.0.

A3 is high density polyethylene with a density of 0.9625 grams/cc, and a melt index of 1.0.

A4 is an ethylene/1-octene elastomer with a density of 0.887 grams/cc, and a melt index of 0.5.

5 A5 is an ethylene/1-octene copolymer with a density of 0.912 grams/cc, and a melt flow index of 1.0.

A6 is an IPN resin with a density of 0.912 grams/cc, and a melt flow index of 1.5.

10 A7 is an IPN resin with a density of 0.917 grams/cc, and a melt flow index of 4.0.

A8 is LLDPE, which in this case is an ethylene/ 1-octene copolymer with a density of 0.920 gm/cc and an octene-1 comonomer content of 6.5%.

A9 is LMDPE, which in this case is an ethylene/1-octene copolymer with a density of 0.935 gm/cc. and an octene-1 comonomer content of 2.5%.

15 A10 is ethylene/vinyl acetate copolymer with 3.3% vinyl acetate monomer, and a melt index of 2.0.

A11 is an ethylene/1-butene elastomer with a density of 0.88 grams/cc, and a melt index of 3.6.

20 A12 is an ethylene/1-butene elastomer with a density of 0.88 grams/cc, and a melt index of 2.2.

A13 is ethylene/vinyl acetate copolymer with 9% vinyl acetate monomer, and a melt index of 2.0.

A14 is an IPN resin with a density of 0.921 grams/cc, and a melt index of 0.76.

A15 is an IPN resin with a density of 0.924 grams/cc, and a melt index of 0.88.

25 A16 is an IPN resin with a density of 0.920 grams/cc, and a melt index of 0.85.

A17 is an IPN resin with a density of 0.9255 grams/cc, and a melt index of 0.85.

A18 is an IPN resin with a density of 0.925 grams/cc, and a melt index of 0.88.

Materials A1, A14, A15, and A18 are further characterized in Table 1A.

Table 1A

	A14	A1	A15	A18
First Component				
polymer split (%)	50	45	50	44
catalyst type	CGC	CGC	CGC	CGC
comonomer type	1-octene	1-octene	1-octene	1-octene
I ₂ melt Index, g/10 min.	0.4	0.3	0.2	0.2
density, g/cc	0.913	0.910	0.915	0.915
GPC M _w /M _n	1.8-2.8	1.8-2.8	1.8-2.8	1.8-2.8
Second Component				
polymer split (%)	50	55	50	56
catalyst type	HEC	HEC	HEC	HEC
comonomer type	1-octene	1-octene	1-octene	1-octene
I ₂ melt Index, g/10 min.	1.3	2.1	10.0	5.0
density, g/cc	0.929	0.9285	0.931	0.930
Polymer Composition				
I ₂ melt Index, g/10 min.	0.76	0.75	0.88	0.88
density, g/cc	0.921	0.92	0.924	0.924
GPC M _w /M _n	2.76	2.7	3.6	3.6
I ₁₀ /I ₂	6.9	7.2	7.6	7.6

These materials are manufactured by Dow Chemical Company in a continuous two-reactor solution polymerization system.

5 "CGC" = constrained geometry catalyst system.

"HEC" = Ziegler heterogeneous high efficiency catalyst system.

"GPC" = gel permeation chromatography.

Examples

10 Examples 1 to 5 of the invention, and the comparative examples ("Co." in the Tables) discussed below, had the structures shown in the Tables, and were each made by a tubular coextrusion of the layers, except that Comparative Examples 10 and 11 (Table 4) were monolayer extruded films. Example 6 is made by a tubular co-extrusion of the layers. Physical property values for Example 6 of Table 6 are predicted values.

15 In the Tables:

* Could not be coextruded.

** These numbers showed a standard deviation of greater than 20% of the average value.

20 ' could not be oriented.

" Natural Centerfold (NCF) line.

''' TM LONG™ stretcher.

"gmf" = grams force

"n" = newton

"J" = Joule

"mil" = 0.001 inches

5 Methodology for generating the physical properties are as indicated in the subscripts in the Tables, corresponding to the following ASTM tests:

¹ ASTM D 882-95 ("Modulus" in the Tables refers to Tensile Modulus).

² ASTM D 1938.

10 ³ ASTM D 2732-83

⁴ ASTM D 3763-95a

^{4a}Values from instrumented impact Peak Load were found via ASTM D 3763-95a.

Values per mil were calculated by normalizing peak load value to gauge.

^{4b}Values from instrumented impact Energy To Break were found via ASTM D 3763-
15 95a. Values per mil were calculated by normalizing energy to break value to gauge.

⁵ ASTM D 1003-95

⁶ ASTM D 1746-92

⁷ ASTM D 2457-90

⁸ ASTM D 2838-95

20 "Melt Index" herein is with reference to ASTM D 1238-90, Condition 190/2.16.

Table 2

Example		Co. 1	Co. 2	Co. 3	Co. 4	Co. 5*
Layer Ratio		15/70/15	15/70/15	15/70/15	15/70/15	15/70/15
Skins		50% A8 + 25% A9 + 25% A10				
Internal		A1	60% A2 + 40% A3	50% A4 + 50% A5	A6	A7
Tensile, LD ¹	(psi)	21931	18297	12933	15459	—
Tensile, TD ¹	(psi)	20687	18982	9657	16225	—
Elongation, LD ¹	(%)	132	109	99	114	—
Elongation, TD ¹	(%)	118	82	88	112	—
Modulus ¹ , LD	(psi)	50640	56470	25970	39620	—
Modulus ¹ , TD	(psi)	51650	62370	22030	40890	—
LD Tear ²						—
Tear, Average	(gmf)	5.96	4.54	11.8	8.8	—
Tear, Maximum	(gmf)	7.38	5.77	20.25**	10.58	—
Energy to Break	(gmf-in)	10.16	7.73	20.76	14.57	—
Gauge	(mil)	0.6	0.565	0.575	—	—
TD Tear ²						—
Tear, Average	(gmf)	5.22	3.98	30.5**	10.3	—
Tear, Maximum	(gmf)	8.89	5.19	57.76**	14.47	—
Energy to Break	(gmf-in)	8.58	7.02	45.25**	18.43	—
Gauge	(mil)	0.585	0.555	0.575	0.66	—
Free Shrink ³						—
200F - LD	(%)	12	15	21	13	—
200F TD	(%)	17	23	25	19	—
220F - LD	(%)	23	27	41	27	—
220F - TD	(%)	34	39	46	35	—
240F - LD	(%)	49	57	66	64	—
240F - TD	(%)	57	63	70	68	—
260F - LD	(%)	79	75	77	79	—
260F - TD	(%)	78	76	75	77	—
280F - LD	(%)	80	79	77	79	—
280F - TD	(%)	79	79	76	77	—
Instrumented Impact ⁴						—
Peak Load	(N)	91.48	79.89	43.44	67.94	—
Energy to Break	(J)	0.78	0.58	0.28	0.51	—
Gauge	(mil)	0.675	0.58	0.455	0.635	—
Peak Load/Mil ^{4a}	(N/mil)	135.5	137.7	95.5	107.0	—
Energy to Break Per Mil ^{4b}	(J/mil)	1.16	1.00	0.62	0.80	—
Haze ⁵	(%)	3.5	4.0	4.0	3.7	—
Clarity ⁶	(%)	80.2	77.9	74.1	80.0	—
Gloss ⁷	(%)	85.0	85.0	82.0	86.0	—
Gauge	(mil)	0.69	0.59	0.54	0.63	—

Table 3

Example		1	Co.6	Co.7	Co.8	Co.9'
Layer Ratio		15/70/15	15/70/15	1/2/1	15/70/15	15/70/15
Skins		50% A1 + 25% A9 + 25% A10	50% A8 + 25% A9 + 25% A10			
Internal		A1	A8	A8	A13	A3
Tensile, LD	(psi)	20387	18254	17681	13867	—
Tensile, TD	(psi)	24548	20850	18583	12065	—
Elongation, LD	(%)	92	78	88	90	—
Elongation, TD	(%)	124	127	124	66	—
Modulus, LD	(psi)	52910	53610	59573	23790	—
Modulus, TD	(psi)	62840	56730	64097	28640	—
LD Tear						
Tear, Average	(gmf)	3.24	3.85	4.15	3.87	—
Tear, Maximum	(gmf)	3.96	4.33		6.1	—
Energy to Break	(gmf-in)	5.48	6.92		6.33	—
Gauge	(mil)	0.645	0.635	0.6	0.55	—
TD Tear						
Tear, 1Average	(gmf)	4.64	4.93	5.625	3.56**	—
Tear, Maximum	(gmf)	5.34	6.29		6.41**	—
Energy to Break	(gmf-in)	8.54	8.22		5.66**	—
Gauge	(mil)	0.64	0.63	0.6	0.51	—
Free Shrink						
200F - LD	(%)	17	15	14	26	—
200F TD	(%)	19	18	17	35	—
220F - LD	(%)	24	21	19	62	—
220F - TD	(%)	28	28	27	65	—
240F - LD	(%)	43	43	40	72	—
240F - TD	(%)	48	50	47	73	—
260F - LD	(%)	79	79	77	80	—
260F - TD	(%)	75	76	73	79	—
280F - LD	(%)	82	81	82	81	—
280F - TD	(%)	77	77	77	80	—
Instrumented Im-						
pact						
Peak Load	(N)	111.16	91.66	90.94	49.91	—
Energy to Break	(J)	1.14	0.85	0.758	0.35	—
Gauge	(mil)	0.635	0.625	0.6	0.555	—
Peak Load Per Mil	(N/mil)	175.1	146.7	151.6	89.9	—
Energy to Break Per Mil	(J/mil)	1.80	1.36	1.26	0.63	—
Haze	(%)	3.5	3.1	3.3	5.0	—
Clarity	(%)	75.6	81.0	77.8	65.8	—
Gloss	(%)	87.2	90.3	85.1	86.0	—
Gauge	(mil)				0.58	—

Table 4

Example		2	Co.10	Co.11	3
Layer Ratio		15/70/15	15/70/15	15/70/15	
Skins		20% A9 + 80% A1	15% A11 + 42.5% A5 +	36% A12 + 27% A5 +	None

			42.5% A10	37% A10	
Internal		A1	A1	A1	A1
Tensile, LD	(psi)	22086	18835	19456	22078
Tensile, TD	(psi)	24251	21684	19112	23162
Elongation, LD	(%)	116	113	131	114
Elongation, TD	(%)	102	130	122	90
Tensile Modulus, LD	(psi)	43840	31030	27920	49720
Tensile Modulus, TD	(psi)	45320	29550	36870	60890
LD Tear					
Tear, Average	(gmf)	4.2	3.84	3.51	4.66
Tear, Maximum	(gmf)	4.73	4.51	4.14	5.24
Energy to Break	(gmf-in)	7.35	7.01	6.39	8.3
Gauge	(mil)	0.62	0.595	0.615	0.59
TD Tear					
Tear, Average	(gmf)	3.06**	4.26	3.47	4.27**
Tear, Maximum	(gmf)	5.21**	5.54	5.2**	5.49
Energy to Break	(gmf-in)	3.44**	7.59	6.6**	7.73**
Gauge	(mil)	0.56	0.645	0.6	0.62
Free Shrink					
200F - LD	(%)	15	14	14	14
200F - TD	(%)	18	17	18	17
220F - LD	(%)	27	30	27	26
220F - TD	(%)	33	37	33	33
240F - LD	(%)	62	64	58	64
240F - TD	(%)	66	66	65	67
260F - LD	(%)	78	80	79	80
260F - TD	(%)	83	80	80	79
280F - LD	(%)	80	79	79	80
280F - TD	(%)	84	80	79	79
Instrumented Impact ^{II}					
Peak Load	(N)	98.71	97.21	90.45	93.96
Energy to Break	(J)	0.85	0.94	0.79	0.94
Gauge	(mil)	0.53	0.655	0.5675	0.56
Peak Load Per Mil	(N/mil)	186.2	148.4	159.4	167.8
Energy To Break Per Mil	(J/mil)	1.60	1.44	1.39	1.68
Instrumented Impact ^{III}					
Peak Load	(N)				97.27
Energy To Break	(J)				1.09
Gauge	(mil)				0.71
Peak Load Per Mil	(N/mil)				137.0
Energy To Break Per Mil	(J/mil)				1.54
Haze	(%)	2.8	6.0	5.0	0.4
Clarity	(%)	83.5	70.8	68.1	89.3
Gloss	(%)	87.0	76.0	77	96.0
Gauge	(mil)	0.49	0.61	0.53	0.57

Table 5

Examples		4
Layer Ratio		15/70/15
Skins		50% A14 + 25% A9 + 25% A10
Internal		90% A14 + 10% HDPE
Tensile, LD	(psi)	25009
Tensile, TD	(psi)	25401
Elongation, LD	(%)	118
Elongation, TD	(%)	101
Modulus, LD	(psi)	70970
Modulus, TD	(psi)	79360
LD Tear		
Tear, Average	(gmf)	4.5
Tear, Maximum	(gmf)	5.19
Energy to Break Gauge	(gmf-in) (mil)	8.48 0.655
TD Tear		
Tear,Average	(gmf)	6.37
Tear,Maximum	(gmf)	12.69
Energy to Break Gauge	(gmf-in) (mil)	11.5 0.66
Free Shrink		
200F - LD	(%)	12
200F TD	(%)	15
220F - LD	(%)	22
220F - TD	(%)	26
240F - LD	(%)	45
240F - TD	(%)	51
Instrumented Impact		
Peak Load	(N)	111.65
Energy to Break Gauge	(J)	1.08
Peak Load Per Mil	(mil)	0.61
Energy To Break Per Mil	(N/mil) (J/mil)	183.0 1.77
Haze	(%)	2.7
Clarity	(%)	84.5
Gloss	(%)	87
Gauge	(mil)	0.60

Table 6

Example		Co.12	5	6
Layer Ratio		15/70/15	15/70/15	15/70/15
Skins		50% A9 + 50% A10	50% A9 + 50% A10	50% A8 + 25% A9 + 25% A10
Internal Gauge		A8	A15	A18
Tensile, LD	(psi)	20103	20500	21000
Tensile, TD	(psi)	23374	24099	23500
Elongation, LD	(%)	118	122	120
Elongation, TD	(%)	95	89	90
Tensile Modulus, LD	(psi)	52050	49150	48000
Tensile Modulus, TD	(psi)	58800	57560	51000
LD Tear				
Tear, Average	(gmf)	4.9	3.9	4.0
Tear, Maximum	(gmf)	5.53	4.48	—
Energy to Break	(gmf-in)	8.63	7.28	—
Gauge	(mil)	0.62	0.59	0.60
TD Tear				
Tear, Average	(gmf)	4.52**	2.39	4.0
Tear, Maximum	(gmf)	5.72**	2.96	—
Energy to Break	(gmf-in)	8.36**	4.24**	—
Gauge	(mil)	0.61	0.59	0.60
Shrink Tension - LD ^b				
200F	(psi)	316.82	313.5	—
220F	(psi)	384.53	362.59	—
240F	(psi)	403.95	404.94	—
260F	(psi)	414.33	403.58	—
280F	(psi)	419.5	403.94	—
Shrink Tension - TD ^b				
200F	(psi)	545.16	598.97	—
220F	(psi)	653.36	694.59	—
240F	(psi)	713.21	710.32	—
260F	(psi)	610.27	650.3	—
280F	(psi)	491.26	552.61	—
Free Shrink - LD				
200F	(%)	13	12	13
220F	(%)	28	25	25
240F	(%)	62	60	62
260F	(%)	79	79	80
280F	(%)	80	80	80
Free Shrink - TD				
200F	(%)	20	19	20
220F	(%)	38	34	36
240F	(%)	67	65	66
260F	(%)	80	80	80
280F	(%)	79	81	80
Instrumented Impact				
Peak Load	(N)	86.3	96.06	—
Energy to Break	(J)	0.73	0.88	—
Gauge	(mil)	0.565	0.565	0.60
Peak Load Per Mil	(N/mil)	152.7	170.0	170.0
Energy To Break Per	(J/mil)	1.29	1.56	1.55

Mil				
Haze	(%)	3.9	4	3.7
Clarity	(%)	84.6	85.3	80
Gloss	(%)	85	85	85
Gauge	(mil)	0.55	0.56	0.6

Table 7

Example		Co.13	Co.14	Co.15
Layer Ratio		Monolayer	Monolayer	Monolayer
Skins		None	None	None
Internal		A8	A16	A17
Instrumented Impact				
- TMLong				
Peak Load	(N)	98.12	46.33	75.17
Energy to Break	(J)	0.75	0.34	0.56
Gauge	(mil)	1.035	0.847	0.99
Peak Load Per Mil	(N/mil)	94.8	54.7	75.93
Energy To Break Per Mil	(J/mil)	0.725	0.401	0.566

** Co.13, Co.14, and Co.15 were not irradiated.

5

Film of the present invention, as well as the comparative films, were made by cast extrusion (for monolayer films) or coextrusion (for multilayer films) by techniques well known in the art. The films were quenched, irradiated by electron beam irradiation at a dosage of between 20 and 35 kiloGrays, and reheated to their orientation temperature, and then stretched by a conventional trapped bubble process. Films were stretched at a ratio of about 5:1 in each of the longitudinal and transverse directions.

10 Film of the present invention can be made by any suitable process, including coextrusion, lamination, extrusion coating, or corona bonding and are preferably made by tubular cast coextrusion, such as that shown in U.S. Patent 4,551,380 [Schoenberg], herein incorporated by reference in its entirety. Bags made from the film can be made by any suitable process, such as that shown in U. S. Patent No. 3,741,253 (Brax et al.), hereby incorporated by reference in its entirety. Side or end sealed bags can be made from single wound or double wound films.

15 20 Film of the present invention can be oriented by any suitable process, including a trapped bubble process or a simultaneous or sequential tenterframe process.

Film of the present invention can have any total thickness desired, so long as the film provides the desired properties for the particular packaging operation in which the film is used. Final film thicknesses can vary, depending on process, end use application, etc. Typical thicknesses range from 0.1 to 20 mils, preferably 0.2 to 15 mils, more preferably 0.3 to 10 mils, more preferably 0.3 to 5 mils, more preferably 0.3 to 2 mils, such as 0.3 to 1 mil.

Film of the present invention can have a tear propagation (ASTM 1938) of between 3 and 10 grams in either or both of the longitudinal and transverse directions.

Film of the present invention can have a haze value of between 0.1 and 5, more preferably between 0.1 and 4.5, more preferably between 0.1 and 4, more preferably between 0.1 and 3.5, more preferably between 0.1 and 3, more preferably between 0.1 and 2.5, and most preferably between 0.1 and 2. Film of the invention can have a haze value of 5 or less than 5, 4 or less than 4, 3.5 or less than 3.5, 3 or less than 3, 2.5 or less than 2.5, 2 or less than 2, or 1 or less than 1.

The multilayer film of the present invention can have a peak load/mil value (ASTM D3763-95a) of at least 155, more preferably at least 160, more preferably at least 165, more preferably at least 167, more preferably at least 170, more preferably at least 175, more preferably at least 180, more preferably at least 185, more preferably at least 190, and most preferably at least 195 newtons/mil. Preferred ranges for peak load/mil are between 155 and 400, more preferably between 155 and 390, more preferably between 160 and 380, more preferably between 165 and 370, more preferably between 167 and 360, more preferably between 170 and 350, more preferably between 175 and 340, more preferably between 180 and 330, more preferably between 185 and 320, more preferably between 190 and 310, and most preferably between 195 and 300 newtons/mil.

The polymeric components used to fabricate film according to the present invention can also contain appropriate amounts of other additives normally included in such compositions. These include slip agents, antioxidants, fillers, dyes, pigments, radiation stabilizers, antistatic agents, elastomers, and other additives known to those of skill in the art of packaging films.

The multilayer film of the present invention can have an energy to break/mil value (ASTM D3763-95a) of at least 1.28, more preferably at least 1.30, more preferably at least 1.35, more preferably at least 1.40, more preferably at least 1.45, more preferably at least 1.50, more preferably at least 1.55, more preferably at least 1.58, more preferably at least 1.60, more preferably at least 1.65, more preferably at least 1.70, more preferably at least 1.75, more preferably at least 1.80, more preferably at least 1.85, and most preferably at least 1.90 Joules/mil. Preferred ranges for energy to break per mil are between 1.28 and 4.00, preferably between 1.30 and 3.00, more preferably between 1.35 and 3.00, more preferably between 1.40 and 2.90, more preferably between 1.45 and 2.85, more preferably between 1.50 and 2.85, more preferably between 1.55 and 2.80, more preferably between 1.60 and 2.75, more preferably between 1.65 and 2.75, more preferably between 1.70 and 2.75, more

preferably between 1.75 and 2.75, and most preferably between 1.80 and 2.50 Joules/mil.

The multilayer film of the present invention exhibits a tensile strength (ASTM D 882-95) of preferably at least 18,000, more preferably at least 19,000, more preferably at least 20,000, more preferably at least 21,000, more preferably at least 21,500, more preferably at least 22,000, more preferably at least 22,500, and most preferably at least 23,000 psi in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions. Preferred ranges for tensile strength are between 18,000 to 200,000, and more preferably between 23,000 and 100,000 psi in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions.

The multilayer film of the present invention exhibits a free shrink (ASTM D 2732-83) at a temperature of 200°F of preferably at least 8%, more preferably at least 9%, more preferably at least 10%, more preferably at least 11%, more preferably at least 13%, and most preferably at least 15% in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions. Preferred ranges for free shrink at a temperature of 200°F are between 8% and 50%, more preferably between 10% and 45%, more preferably between 15% and 40% in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions.

The multilayer film of the present invention exhibits a composite free shrink at a temperature of 200°F of preferably at least 16%, more preferably at least 18%, more preferably at least 20%, more preferably at least 25%, and most preferably at least 30%. Preferred ranges for composite free shrink at a temperature of 200°F are between 16% and 100%, more preferably between 20% and 90%, more preferably between 25% and 75%, and most preferably between 30% and 70%.

The multilayer film of the present invention exhibits a free shrink balance at a temperature of 240°F (115°C) of preferably less than or equal to 30%, more preferably less than 20%, more preferably less than 15%, more preferably less than 10%, and most preferably less than 5%. Preferred ranges for free shrink balance at a temperature of 240°F are between 0% and 30%, more preferably between 0% and 20%, more preferably between 0% and 15%, more preferably between 0% and 10%, and most preferably between 0% and 5%.

The multilayer film of the present invention can be stretch oriented at stretching ratios of preferably at least about 1.5:1, more preferably at least about 2:1, more preferably at least about 2.5:1, more preferably at least about 3:1, more preferably at least

about 3.25:1, more preferably at least about 3.5:1, more preferably at least about 4:1, more preferably at least about 4.5:1, and most preferably at least about 5:1 in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions. Preferred ranges for stretch orientation ratios are

5 preferably between 1.5:1 and 8:1, more preferably between 3:1 and 7:1, and most preferably between 4:1 and 6:1 in either or both of the longitudinal and transverse directions, and preferably in both the longitudinal and transverse directions.

The multilayer film of the present invention is preferably crosslinked, by chemical means or, preferably, by irradiation such as by electron beam irradiation at a dose of between 10 and 200, more preferably between 15 and 150, more preferably between 20 and 150, and most preferably between 20 and 100 kiloGray. Although the invention does not have to be irradiated, in a preferred embodiment, irradiation can be used to improve impact strength. IPN resins suitable for use in the present inventive films have a melt index of preferably between 0.1 and 1.4, more preferably between 10 15 0.3 and 1.3, more preferably between 0.4 and 1.2, most preferably between 0.5 and 1.0, such as between 0.6 and 1.0. Preferably, the film has a substantially balanced free shrink.

Preferably, at least 50% by volume of the total film volume comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 20 1.4.

In preferred IPN resins, the homogeneous component forms between 44% and 49% by weight of the resin, and the heterogeneous component forms between 51% and 56% by weight of the resin. In preferred IPN resins, the homogeneous component forms less than 50% by weight of the resin, and the heterogeneous component forms 25 more than 50% by weight of the resin. In preferred IPN resins, the heterogeneous component has a melt index between 6 and 50 times greater than the melt index of the homogeneous component.

It is to be understood that variations of the present invention can be made 30 without departing from the scope of the invention, which is not limited to the specific embodiments and examples disclosed herein.

What is claimed is:

1. A multilayer oriented heat shrinkable film comprising:
 - a) an internal layer comprising a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin comprising
 - i) a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and
 - ii) a heterogeneous component with a melt index of between 1.5 and 20; and
 - b) outer layers comprising a polymeric resin;
wherein the film has
 - i) a haze value (ASTM D 1003-95) less than or equal to 5,
 - ii) a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and
 - iii) a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.
- 20 2. The film of claim 1 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 is derived from a solution mixture of homogeneous ethylene/ alpha-olefin and heterogeneous ethylene/ alpha-olefin.
- 25 3. The film of claim 1 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin is produced from a solution polymerization of homogeneous ethylene/ alpha-olefin and solvent combined with a solution polymerized heterogeneous ethylene/ alpha-olefin.
- 30 4. The film of claim 1 wherein the homogeneous ethylene/alpha-olefin component is long chain branched.
5. The film of claim 1 wherein the outer layers each comprise a polymeric resin selected from the group consisting of
 - i) ethylene/alpha olefin copolymer,
 - ii) ethylene/vinyl acetate copolymer,

- iii) ethylene/alkyl acrylate copolymer,
- iv) ethylene/acrylic acid copolymer,
- v) ionomer,
- vi) propylene polymer and copolymer,
- 5 vii) butylene polymer and copolymer,
- viii) multicomponent ethylene/alpha-olefin interpenetrating network resin different in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer, and
- ix) a blend of the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer with another polymeric resin.

10

- 6. The film of claim 1 wherein the film has a substantially balanced free shrink.
- 7. The film of claim 1 wherein at least 50% by volume of the total film volume
15 comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.
- 8. A multilayer oriented heat shrinkable film comprising:
 - a) an internal layer comprising polymeric resin;
 - 20 b) first and second intermediate layers, each disposed on a respective opposite side of the internal layer, comprising multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, the resin comprising
 - i) a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and
 - 25 ii) a heterogeneous component with a melt index of between 1.5 and 20; and
 - c) first and second outer layers, disposed on the first and second intermediate layers respectively, comprising a polymeric resin;
- 30 wherein the film has
 - i) a haze value (ASTM D 1003-95) less than or equal to 5,
 - ii) a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and
 - 35 iii) a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.

9. The film of claim 8 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 is derived from a solution mixture of homogeneous ethylene/ alpha-olefin and heterogeneous ethylene/ alpha-olefin.

5

10. The film of claim 8 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin is produced from a solution polymerization of homogeneous ethylene/ alpha-olefin and solvent combined with a solution polymerized heterogeneous ethylene/ alpha-olefin.

10

11. The film of claim 8 wherein the homogeneous ethylene/alpha-olefin component is long chain branched.

15

12. The film of claim 8 wherein the internal and outer layers each comprise a polymeric resin selected from the group consisting of

20

- i) ethylene/alpha olefin copolymer,
- ii) ethylene/vinyl acetate copolymer,
- iii) ethylene/alkyl acrylate copolymer,
- iv) ethylene/acrylic acid copolymer,
- v) ionomer,
- vi) propylene polymer and copolymer,
- vii) butylene polymer and copolymer,
- viii) multicomponent ethylene/alpha-olefin interpenetrating network resin different in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin of the intermediate layers, and
- ix) a blend of the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer with another polymeric resin..

25

13. The film of claim 8 wherein the intermediate layers can each further comprise a polymeric resin selected from the group consisting of

30

- i) ethylene/alpha olefin copolymer,
- ii) ethylene/vinyl acetate copolymer,
- iii) ethylene/alkyl acrylate copolymer,
- iv) ethylene/acrylic acid copolymer,
- v) ionomer,
- vi) propylene polymer and copolymer,

- vii) butylene polymer and copolymer, and
- viii) a second multicomponent ethylene/alpha-olefin interpenetrating network resin.

5 14. The film of claim 8 wherein the film has a substantially balanced free shrink.

15. The film of claim 8 wherein at least 50% by volume of the total film volume comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

10

16. A solid state oriented heat shrinkable film comprising:

- a) between 50 and 100 percent, by volume of the total film, of a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, , the resin comprising
 - i) a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and
 - ii) a heterogeneous component with a melt index of between 1.5 and 20; and
- b) between 0 and 50 percent, by volume of the total film, of a polymeric

20 resin;

wherein the film has

- i) a haze value (ASTM D 1003-95) less than or equal to 5,
- ii) a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and
- 25 iii) a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.

17. The film of claim 16 wherein the film is a multilayer film.

30

18. The film of claim 16 wherein the polymeric resin is different in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

35 19. The film of claim 16 wherein the film has a substantially balanced free shrink.

20. The film of claim 16 wherein at least 50% by volume of the total film volume comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

5 21. The film of claim 16 wherein the film comprises between 1% and 10% by volume of the total film, of the polymeric resin; and between 99% and 90%, by volume of the total film, of the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

10 22. The film of claim 16 wherein the polymeric resin is selected from the group consisting of:

- i) ethylene/alpha olefin copolymer,
- ii) ethylene/vinyl acetate copolymer,
- iii) ethylene/alkyl acrylate copolymer,

15 iv) ethylene/acrylic acid copolymer,

- v) ionomer,
- vi) propylene polymer and copolymer, and
- vii) butylene polymer and copolymer.

20 23. The film of claim 16 wherein the film has substantially balanced free shrink.

24. A multilayer oriented heat shrinkable film comprising:

25 a) an internal layer comprising a blend of a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4, and ethylene polymer or copolymer having a density of at least 0.935 grams/cubic centimeter, wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 comprises

- i) a homogeneous component having a melt index of less than 1, and a density of at least 0.91 grams/cubic centimeter, and

30 ii) a heterogeneous component with a melt index of between about 1.0 and 20; and

- b) outer layers comprising a polymeric resin;

wherein the film has

- i) a haze value (ASTM D 1003-95) less than or equal to 5,

35 ii) a peak load/mil value (ASTM D 3763-95a) of at least 155 newtons/mil, and

- iii) a free shrink (ASTM D 2732-83) at a temperature of 200°F of at least 8% in either or both of the longitudinal and transverse directions.

5 25. The film of claim 24 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4 is derived from a solution mixture of homogeneous ethylene/ alpha-olefin and heterogeneous ethylene/ alpha-olefin.

10 26. The film of claim 24 wherein the multicomponent ethylene/alpha-olefin interpenetrating network resin is produced from a solution polymerization of homogeneous ethylene/ alpha-olefin and solvent combined with a solution polymerized heterogeneous ethylene/ alpha-olefin.

15 27. The film of claim 24 wherein the homogeneous ethylene/alpha-olefin component is long chain branched.

28. The film of claim 24 wherein the outer layers each comprise a polymeric resin selected from the group consisting of

20 i) ethylene/alpha olefin copolymer,
ii) ethylene/vinyl acetate copolymer,
iii) ethylene/alkyl acrylate copolymer,
iv) ethylene/acrylic acid copolymer,
v) ionomer,

25 vi) propylene polymer and copolymer,
vii) butylene polymer and copolymer,
viii) multicomponent ethylene/alpha-olefin interpenetrating network resin different in composition from the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer, and

30 ix) a blend of the multicomponent ethylene/alpha-olefin interpenetrating network resin of the internal layer with another polymeric resin.

29. The film of claim 24 wherein the film has a substantially balanced free shrink.

30. The film of claim 24 wherein at least 50% by volume of the total film volume comprises a multicomponent ethylene/alpha-olefin interpenetrating network resin having a melt index less than 1.4.

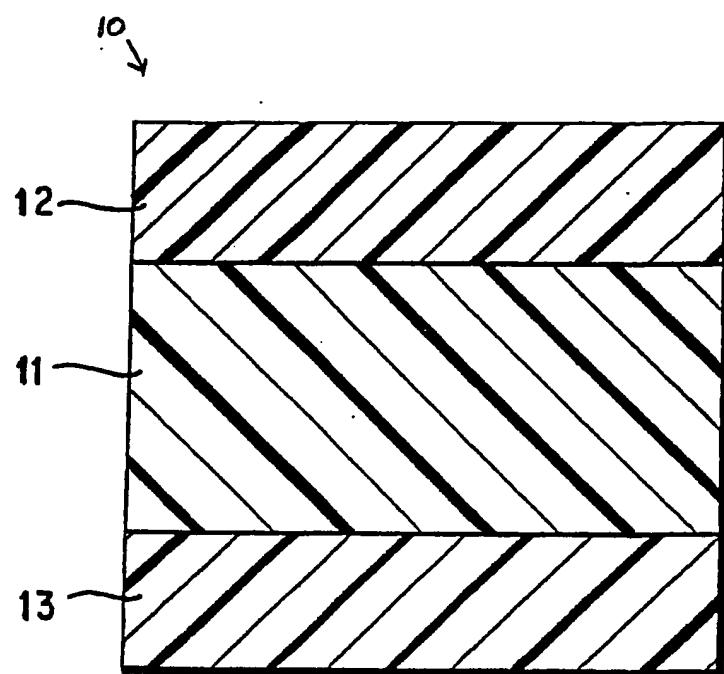


FIG.1

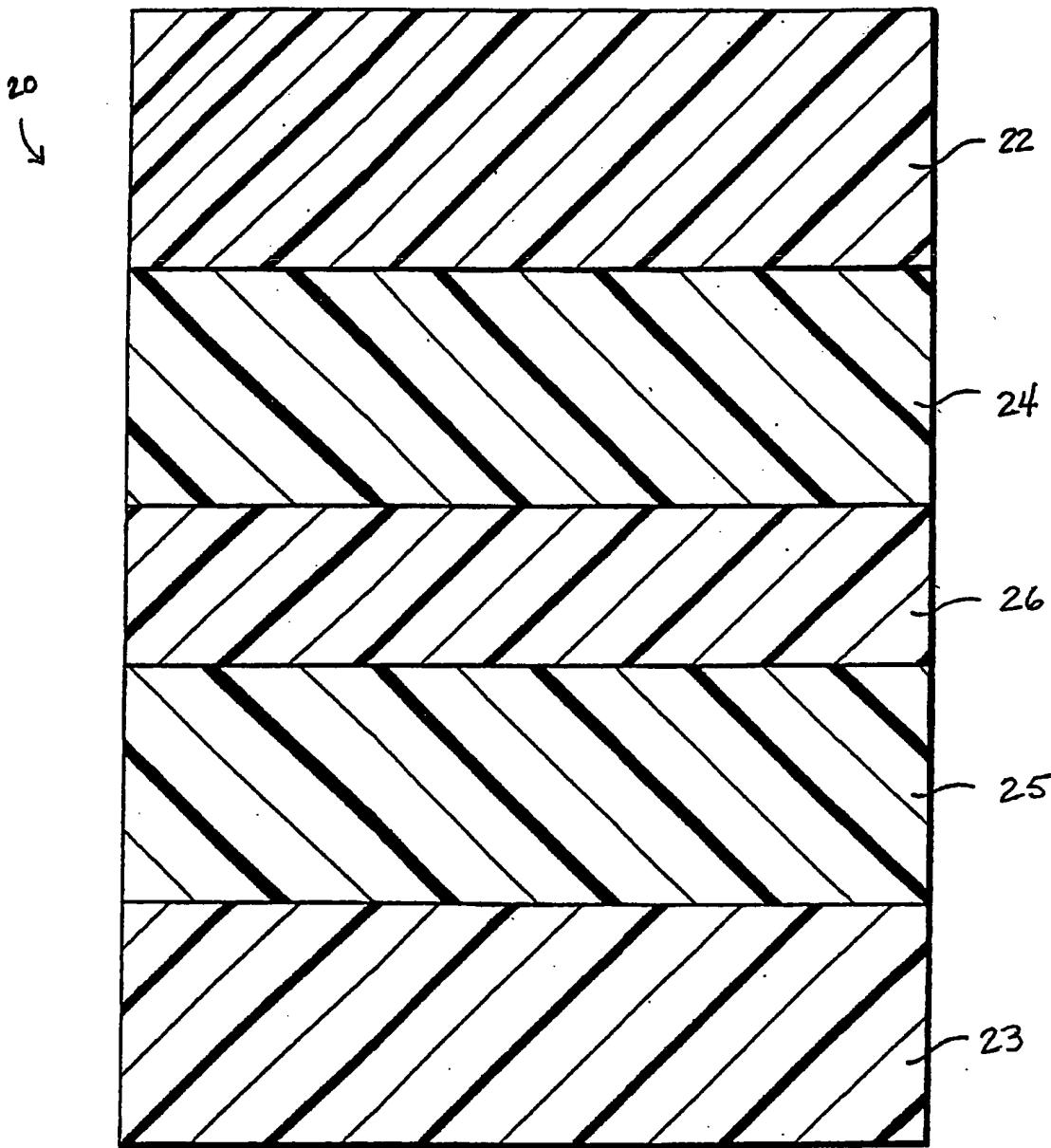


FIG. 2

FIG. 3

CRYSTAF Results

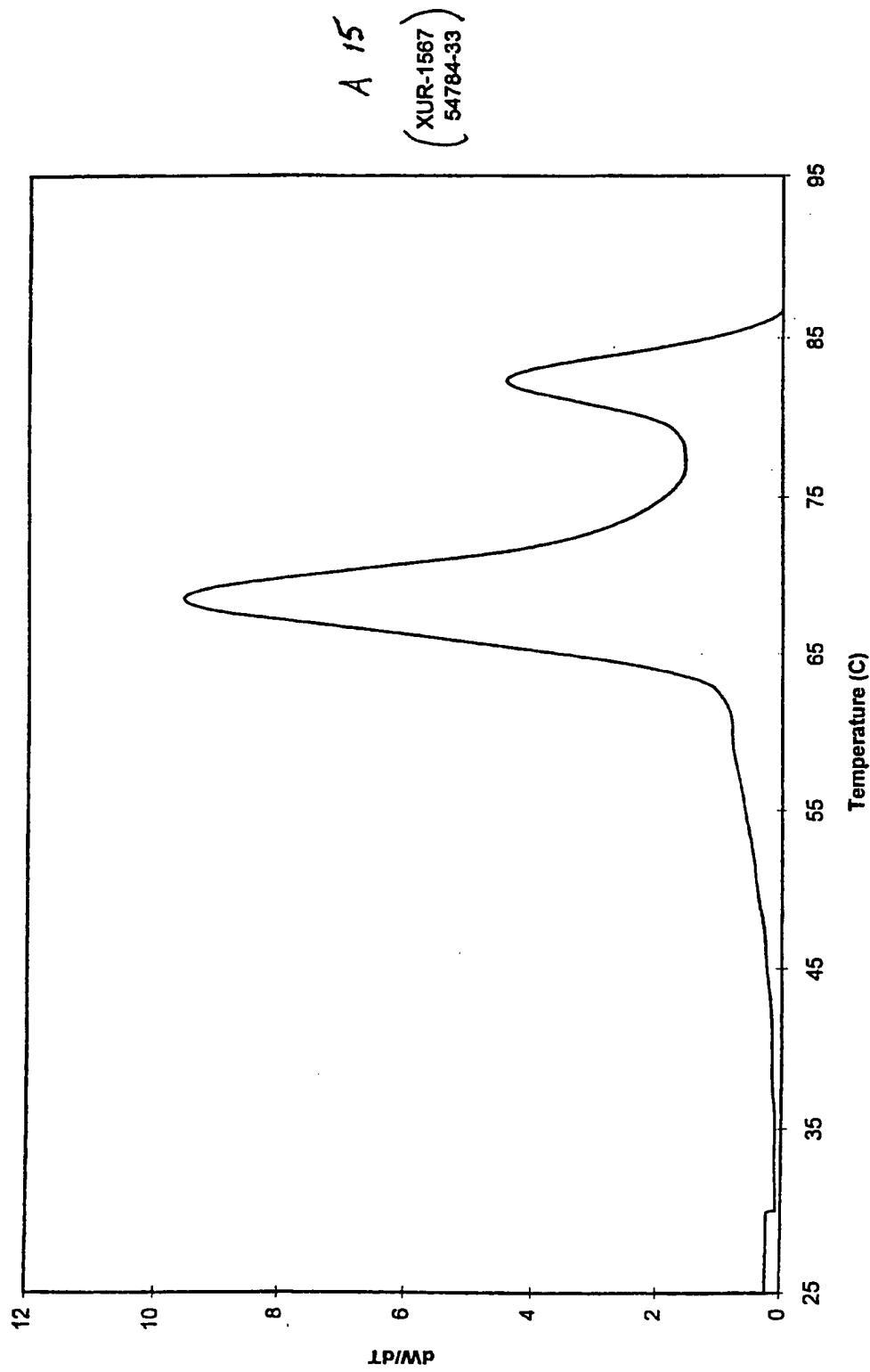


FIG. 4

CRYSTAF Results

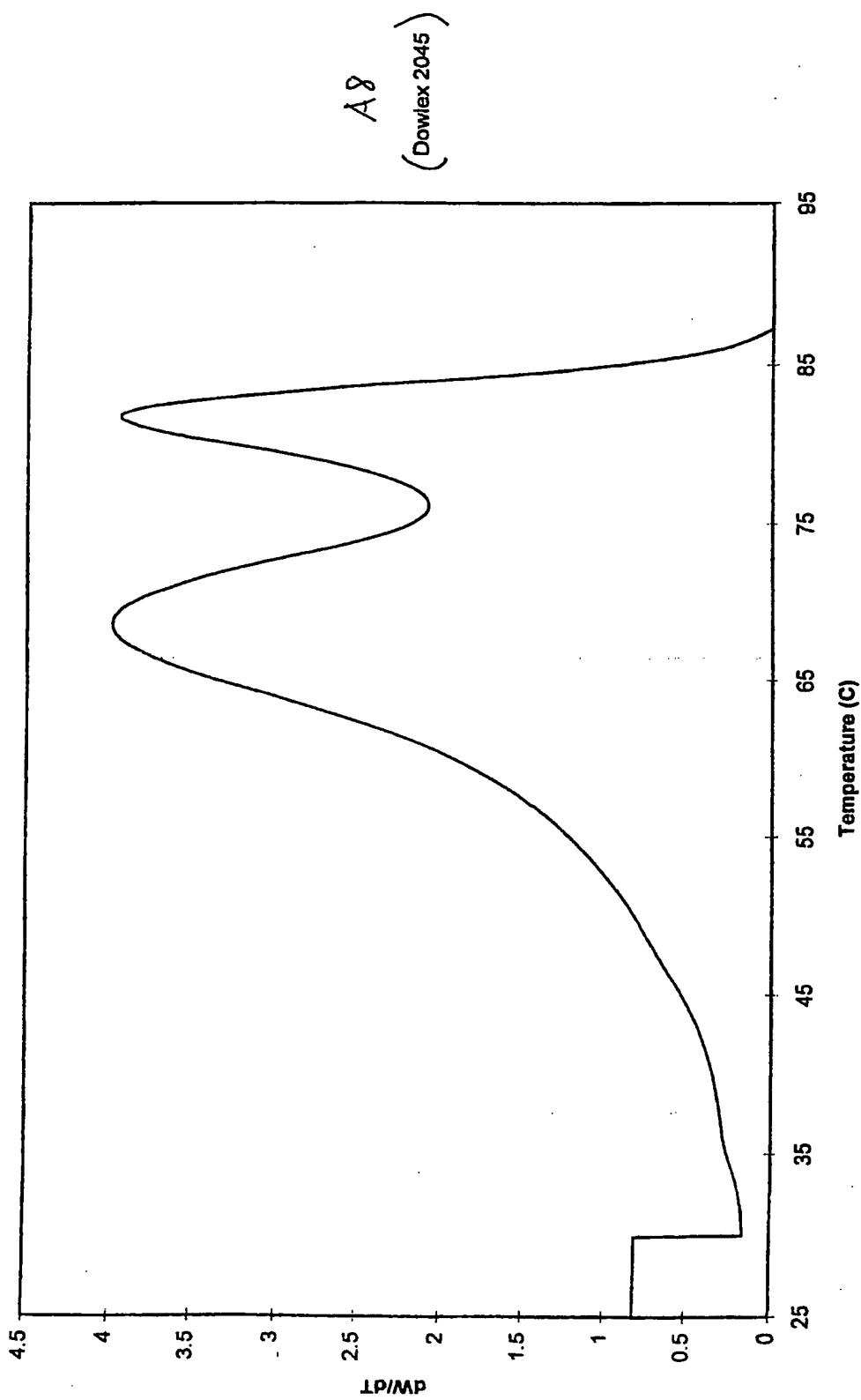


Fig. 5

CRYSTAF Results

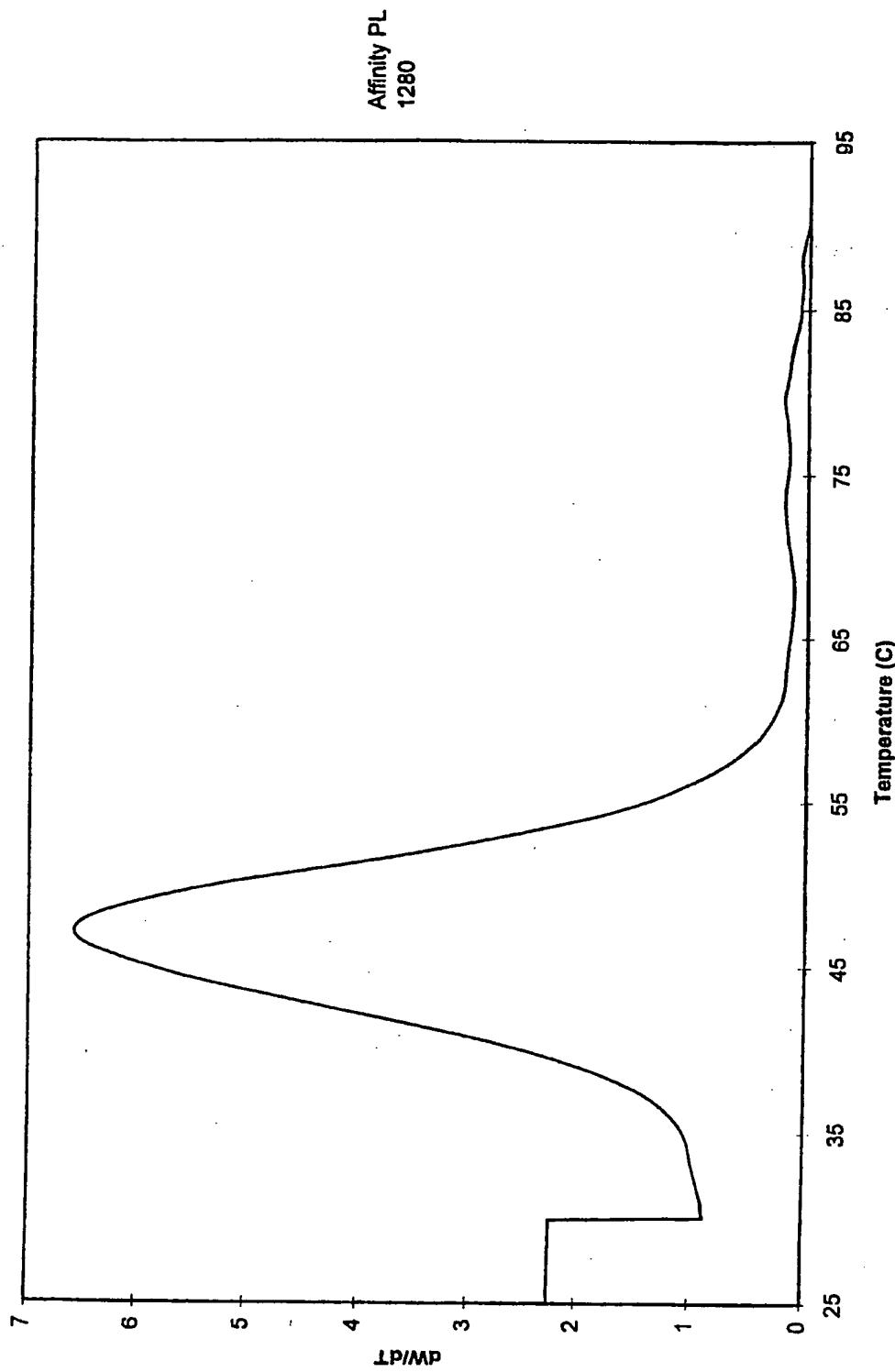
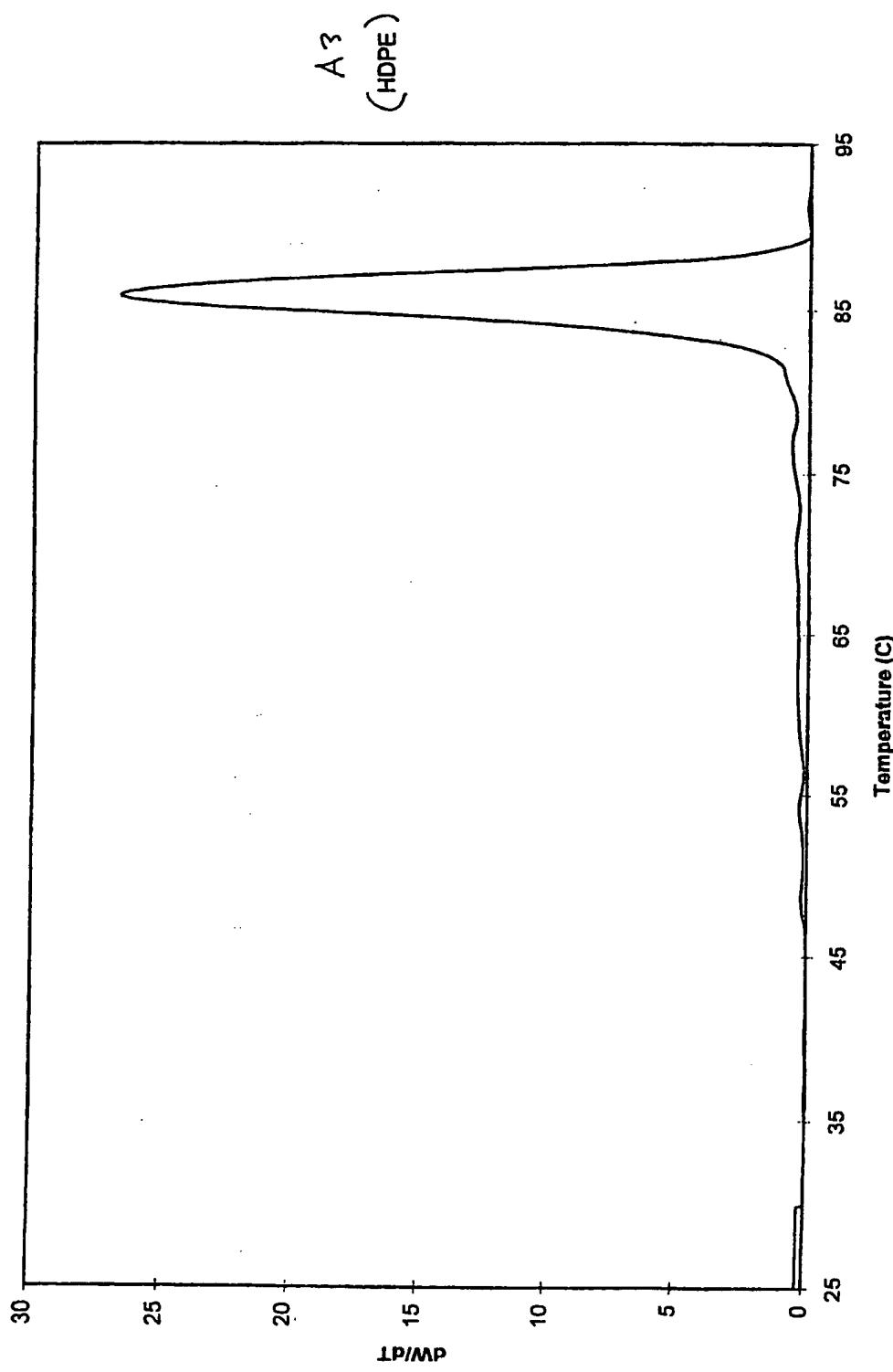


Fig. 6

HD9659 - CRYSTAF Results



INTERNATIONAL SEARCH REPORT

Internatc Application No
PCT/US 00/21483

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B32B27/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 747 594 A (DEGROOT JACQUELYN A ET AL) 5 May 1998 (1998-05-05) cited in the application column 4, line 55 -column 5, line 31 column 14, line 4 - line 6 column 14, line 17 - line 19 column 17, line 30 - line 49 column 18, line 16 - line 21 examples ----- WO 94 25523 A (DOW CHEMICAL CO) 10 November 1994 (1994-11-10) page 1, line 32 -page 2, line 22 page 3, line 3 -page 4, line 3 page 15, line 17 - line 20 ----- -/-	16-23 1-7, 16-23

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

Z document member of the same patent family

Date of the actual completion of the international search

24 October 2000

Date of mailing of the international search report

03/11/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentdaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De Jonge, S

1

BEST AVAILABLE COPY

INTERNATIONAL SEARCH REPORT

Internatc Application No

PCT/US 00/21483

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 26000 A (DUN JOZEF J VAN ;DEGROOT JACQUELYN A (US); SEHANOBISH KALYAN (US);) 18 June 1998 (1998-06-18) page 6, line 20 -page 8, line 5 -----	16-23

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internatc	Application No
PCT/US 00/21483	

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5747594	A 05-05-1998	AU 685331	B	15-01-1998
		AU 3947195	A	15-05-1996
		BR 9510388	A	23-12-1997
		CA 2203128	A	02-05-1996
		CN 1167496	A	10-12-1997
		EP 0787167	A	06-08-1997
		FI 972169	A	21-05-1997
		JP 10507786	T	28-07-1998
		NO 971819	A	18-06-1997
		NZ 295837	A	29-06-1999
		WO 9612762	A	02-05-1996
		US 5582923	A	10-12-1996
		US 5792534	A	11-08-1998
		US 5773155	A	30-06-1998
		US 5773106	A	30-06-1998
		US 5874139	A	23-02-1999
		US 5863665	A	26-01-1999
WO 9425523	A 10-11-1994	AT 174945	T	15-01-1999
		AU 676047	B	27-02-1997
		AU 6638894	A	21-11-1994
		BR 9406668	A	23-01-1996
		CN 1121730	A	01-05-1996
		CZ 9502830	A	15-05-1996
		DE 69415518	D	04-02-1999
		DE 69415518	T	20-05-1999
		DK 696300	T	23-08-1999
		EP 0696300	A	14-02-1996
		ES 2125452	T	01-03-1999
		FI 955148	A	27-10-1995
		HU 72909	A, B	28-06-1996
		JP 2894517	B	24-05-1999
		JP 8509767	T	15-10-1996
		NO 954327	A	22-12-1995
		NZ 265562	A	24-10-1997
		PL 311306	A	05-02-1996
		SI 9420032	A	30-04-1996
		US 5677383	A	14-10-1997
		US 5847053	A	08-12-1998
		US 6111023	A	29-08-2000
		ZA 9402902	A	26-10-1995
WO 9826000	A 18-06-1998	AU 7400598	A	03-07-1998
		CN 1245513	A	23-02-2000
		EP 0944669	A	29-09-1999
		ZA 9711155	A	11-06-1999